

# **ELECTRONIC ELEMENT**

## **BACKGROUND OF THE INVENTIONS**

### **FIELD OF THE INVENTION**

The present invention relates to an electronic element, and, more particularly, to an electronic element used as a cold cathode element that emits electrons with application of an electric field.

### **DESCRIPTION OF THE RELATED ART**

Hot and cold cathode elements are conventionally known as electron emitting elements.

The hot cathode element, which can be represented by a vacuum tube, suffers from a problem that it is difficult to integrate, because of the heat produced. On the other hand, the cold cathode element can be applied to a flat panel display, a voltage amplifying element, a high frequency amplifying element and the like as an element which is capable of being integrated, since heat is not used.

### **SUMMARY OF THE INVENTION**

Accordingly, it is an object of the present invention to provide an electronic element of the above-described type, which has a high practicality, e.g., a capability to emit electrons sufficiently even when only a low voltage is applied, for example, when it is used as a cold cathode element.

To achieve the above object, according to an exemplary embodiment of the present invention, there is provided an electronic element which is formed of a deposited film containing cesium (Cs) and having a plurality of projections made of cesium oxide on a surface thereof.

Cesium (Cs) is the largest in ion radius (0.181 nm) and in metallic bond radius (0.266 nm) among elements. Therefore, if cesium is present in the vapor-deposited film, a distortion is produced in the film, such that the electric insulating properties of the deposited film, namely, of the electronic element can be reduced, on the one hand, while the electric conductivity of the deposited film can be increased, on the other hand. Cesium is present at a plurality of points not only contained inside of the deposited film, but also on the surface of the deposited film. In this case, cesium present on the surface of the film combines with oxygen in the air to form stable cesium oxide, since cesium is active. The cesium oxide is extremely fine, but forms projections.

In a cold cathode element including such an electronic element, the electric field emitted from the element is reduced and hence, even if the voltage applied to the cold cathode element is lowered, a sufficient emission of electrons can be realized.

According to the present invention, there is also provided an electronic element comprising a main body which is formed of an amorphous film of carbon and contains a metal element having a metallic bond radius equal to or larger than two times the atom radius of carbon (C),

and a surface layer which covers the main portion and is formed of an amorphous film of carbon having a high  $sp^3$  hybridization.

If the metal element having a metallic bond radius as described above is present in the main body formed of the amorphous film of carbon, a distortion is produced in the inside of the main body. Thus, the electric insulating property of the main body can be reduced, on the one hand, while the electric conductivity of the main body can be increased, on the other hand. The amorphous film of carbon constituting the surface layer and having the high  $sp^3$  hybridization originally has an excellent electric-field emitting characteristic. In a cold cathode element including such an electric element, the electric field emitted from the element is lowered and hence, even if the voltage applied to the cold cathode element is lowered, a sufficient emission of electrons can be realized.

The above and other objects, features and advantages of the invention will become apparent from the following description of the preferred embodiments taken in conjunction with the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 is a sectional view of a first exemplary embodiment of a cathode unit according to the present invention;

Fig.2 is a diagrammatic illustration of an ultra-high vacuum type negative ion beam depositing apparatus;

Fig.3 is a beam spectrum provided by the apparatus shown in Fig.2;

Fig.4 is a chart showing results of a Raman spectroscopic analysis of an amorphous film of carbon;

Fig.5 is a photograph of the surface of the amorphous film of carbon by an interatomic force microscope;

Fig.6 is an enlarged tracing of an essential portion of the surface shown in Fig.5;

Fig.7 is a view for explaining an emitted electric field measuring method;

Fig.8 is a sectional view of a second exemplary embodiment of a cathode unit according to the present invention;

Fig.9 is a photoelectron spectrum of  $C_{1s}$  electron by an X-ray photoelectron spectroscopic analysis conducted for a surface layer of the cathode unit;

Fig.10 is a view of a main body of the cathode unit immediately after being formed;

Fig.11 is a view of the main body after being changed with the passage of time;

Fig.12 is a sectional view of a third exemplary embodiment of a cathode unit according to the present invention;

Fig.13 is a photograph of the surface of a surface layer by an interatomic force microscope; and

Fig.14 is an enlarged tracing of an essential portion of the surface shown in Fig.13.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will now be described by way of exemplary embodiments with reference to the accompanying drawings.

Fig.1 shows a first embodiment of an exemplary cathode unit 1. The cathode unit 1 is comprised of a cathode plate 2 made of, for example, aluminum (Al), and a cold cathode element 3 as an electronic element, which is formed on a surface of the cathode plate 2. The cold cathode element 3 is formed of a vapor-deposited film containing cesium and has a plurality of very fine conical projections 4 composed of cesium oxide on the surface thereof. The deposited film is, for example, an amorphous film of carbon, in this embodiment, and the conical projections 4 have, for example, an average height  $h$  in a range of  $10\text{ nm} \leq h \leq 500\text{ nm}$  and, preferably, in a range of  $10\text{ nm} \leq h \leq 100\text{ nm}$ ; and more preferably in a range of  $20\text{ nm} \leq h \leq 60\text{ nm}$ .

Cesium (Cs) is the largest in ion radius (0.181 nm) and in metallic bond radius (0.266 nm) among elements. Therefore, if cesium is present in the amorphous film of carbon, a distortion is produced in the inside of the film. Thus, the electric insulating property of the amorphous film of carbon, namely, the cold cathode element 3 can be reduced, on the one hand, while the electric conductivity of the cold cathode element 3, can be increased, on the other hand. Cesium is present at a plurality of points not only within the deposited film, but also on the surface of the deposited film. Active cesium on the surface of the film combines with oxygen in the air

to form stable cesium oxide. The cesium oxide is extremely fine, but forms the conical projections 4. Further, cesium in the film has the effect of decreasing the work function of carbon (C).

In such a cold cathode element 3, the electric field emitted from the element 3 is lowered and hence, even if the voltage applied to the cold cathode element 3 is lowered, a sufficient emission of electrons can be realized.

However, if the average height  $h$  of the conical projections 4 is smaller than 10 nm, no effect is provided. On the other hand, if the average height  $h$  of the conical projections 4 is larger than 500 nm, the distortion in the surface of the element and in the vicinity thereof is increased, and as a result, cracks are liable to be produced in the cold cathode element 3.

In order to provide an effect as described above, it is preferable that the content of Cs in the amorphous film of carbon is set, for example, in a range of  $0.1 \% \text{ by atom} \leq \text{Cs} \leq 5.0 \% \text{ by atom}$  and, preferably, in a range of  $0.5\% \text{ by atom} \leq \text{Cs} \leq 2.0\% \text{ by atom}$  and, more preferably, in a range of  $.75\% \text{ by atom} \leq \text{Cs} \leq 1.25\% \text{ by atom}$ . In this case, if the Cs content is smaller than 0.1 % by atom, the cesium has little or no effect. On the other hand, if the Cs content is larger than 5.0 % by atom, the distortion in the film is too large, and as a result, the  $sp^3$  hybridization of the film is reduced. For this reason, the emission of an electric field by the affinity of the film for negative electrons cannot be expected.

The amorphous film of carbon may be used as a simple component and moreover, may be also used as a material for forming a layer for covering the surface of, for example, a cold cathode element made of silicon in order to enhance the performance of the cold cathode element.

The amorphous film of carbon can be formed by an ion beam depositing process. In forming the amorphous film of carbon, cesium can be contained uniformly in the amorphous film of carbon by using cesium ions as incident ions and by regulating the forming conditions. In the ion beam deposition process, a positive or negative ion beam can be used. In this case, the density of atoms forming the amorphous film of carbon becomes higher in the order of those provided by the positive ion beam deposition process and the negative ion beam deposition process. Namely, the electric conductivity becomes higher in this order, and the electric field emitted becomes lower in this order. Such a difference between densities of atoms is due to the reason that the internal potential energy (electron affinity) of negative ions is lower than the internal potential energy (ionization potential) of positive ions.

Particular examples will be described below.

Fig.2 shows a known ultra-high vacuum type negative ion beam depositing apparatus (e.g., a neutral and ionized alkaline metal bombardment type heavy negative ion source(NIABNIS)). This apparatus includes a cesium plasma ion source 8 having a center anode pipe 5, a filament 6, thermal shields 7 and the like, a suppressor 9, a target





Table 1

Amorphous film of carbon	Deposition voltage (V)	Extracting voltage (kV)	Voltage-current (V-A) of filament
Example A1	500	8	10.7-20.2
Example A2	200	7	8.6-17.6
Example A3	200	9	9.5-18.0
Example A4	500	8	13.2-22.4

Then, substantially central portions of the examples A1 to A4 were subjected to a Raman spectroscopic analysis to examine whether they were amorphous. Fig.4 shows a result of the analysis of the example A2, where a broad Raman band about the vicinity of a wavelength equal to  $1,500\text{ cm}^{-1}$  is observed. It was ascertained from this result that the example A2 was amorphous. In the cases of the other examples A1, A3 and A4, results similar to that in Fig.4 were obtained.

The content of Cs in each of the examples A1 to A4 was examined by an XPS (X-ray Photoelectron Spectroscopy) quantitative analysis. As a result, it was ascertained that each of the examples A1 to A3 contained cesium (Cs), but that the example A4 contained no cesium.

Further, photographs of surfaces of the examples A1 to A4 were taken by an interatomic force microscope (AFLM). Fig.5 is the photograph of the surface of the example A2, and Fig.6 is an enlarged tracing of an essential portion of the surface of the example A2. In these Figures, a large number of conical projections 4 dotted on the surface of the

amorphous film 3 of carbon are formed of cesium oxide. In the cases of the other examples A1 and A3, results similar to that shown in Fig.5 were obtained. An average height  $h$  of the conical projections 4 in each of the examples A1 to A3 was determined from these photographs of the surfaces.

Further, the measurement of the electric field emitted in each of the examples was carried out by a method shown in Fig.7. More specifically, a conductive plate 19 of aluminum was connected to a voltage-regulatable power source 18, and a cover glass sheet 21 having a thickness of 150  $\mu\text{m}$  and provided at its central portion with an opening 20 having a length of 0.8 cm and a width of 0.8 cm (an area of 0.64  $\text{cm}^2$ ) was placed onto the conductive plate 19. An amorphous film of carbon 3 of a cathode unit 1 was placed onto the cover glass sheet 21 and further, an ammeter 22 was connected to the cathode plate 2. Then, a predetermined value of voltage was applied from the power source 18 to the conductive plate 19, and a value of current was read by the ammeter 22. An emitted current density ( $\mu\text{A}/\text{cm}^2$ ) was determined from the measured value of current and the area of the opening 20. When the emitted current density reached 8  $\mu\text{A}/\text{cm}^2$ , the emitted electric field ( $\text{V}/\mu\text{m}$ ) was determined from the voltage corresponding to such emitted current density and the thickness of the cover glass sheet 21.

Table 2 shows the Cs content, the average height  $h$  of the conical projections 4 and the emitted electric field for each of the examples A1 to A4.

Table 2

Amorphous film of carbon	Cs content (% by atom)	Average height $h$ (nm) of conical projections	Emitted electric field (V/ $\mu$ m)
Example A1	1.2	60	0.91
Example A2	0.98	45	1.3
Example A3	0.78	20	3.2
Example A4	0	-	9.3

As apparent from Table 2, the emitted electric field in each of the examples A1 to A3 having the plurality of projections formed of Cs oxide on the surface thereof is extremely low, as compared with the example A4 having no projection 4.

Fig.8 shows a second exemplary embodiment of a cathode unit 1. The cathode unit 1 is comprised of a cathode plate 2 of aluminum, and a cold cathode element 3 as an electronic element which is formed on a surface of the cathode plate 2. The cold cathode element 3 includes a main body 3a which is formed of an amorphous film of carbon and contains a metal element 23 having a metallic bond radius equal to or larger than two times the atom radius of carbon (C), and a surface layer 3b which is bonded to the main body 3a and formed of an amorphous film of carbon

having a high  $sp^3$  hybridization.

If the metal element 23 having the above-described metallic bond radius is present in the main body 3a formed of the amorphous film of carbon, a distortion is produced in the inside of the main body 3a. Thus, the electric insulating property of the main body 3a can be reduced, on the one hand, while the electric conductivity of the main body 3a can be increased, on the other hand. The metal element 23 is also present at a plurality of points at an interface 24 of the main body 3a to the surface layer 3b. In this case, the metal element 23 in the interface 24 combines with oxygen in the air to form a stable oxide, because the metal element 23 is active. The oxide is extremely fine, but produces projections 4. As a result, the surface layer 3b has a plurality of protrusions 25 that conform to the projections 4. The amorphous film of carbon forming the surface layer 3b and having the high  $sp^3$  hybridization originally has an excellent electric field emitting characteristic. An electric field concentrating effect is applied to the amorphous film of carbon by the protrusions 25 and hence, the electric field emitting characteristic of the surface layer 3b is further enhanced.

In such a cold cathode element 3, the electric field emitted therefrom is lowered. Therefore, even if the voltage applied to the cold cathode element 3 is lowered, a sufficient emission of electron can be realized.

The atom radius of carbon is 0.077 nm and hence, cesium (Cs) having a metallic bond radius of 0.266 nm, rubidium (Rb) having a metallic

bond radius of 0.247 nm and the like may be used as the metal element 23.

In the surface layer 3b, it is desirable that a half-value width  $Hw$  of a photoelectron spectrum of  $C_{1s}$  electron by an X-ray photoelectron spectroscopic analysis (ESCA, XPS) is equal to or smaller than 2.0 eV ( $Hw \leq 2.0$  eV). The half-value width  $Hw$  is determined from the photoelectron spectrum of  $C_{1s}$  electrons obtained by carrying out the X-ray photoelectron spectroscopic analysis of the surface layer 3b. Namely, the spectrum width (eV) which is one half of a peak value is defined as the half-value width  $Hw$ . If the half-value width  $Hw$  is set at a value as described above in the surface layer 3b, the emitted electric field can be lowered.

The amorphous film of carbon having a two-layer configuration is also used as a material for forming a surface covering layer, for example, of a cold cathode element made of silicon (Si) in order to enhance the performance of the cold cathode element.

The main body 3a and the surface layer 3b are formed by an ion beam deposition process. In forming each of the main body 3a and the surface layer 3b, cesium ions are used as incident ions, and cesium used as the metal element 23 can be contained uniformly in the main body 3a by regulating the forming conditions. In the ion beam deposition process, a positive or negative ion beam may be used. In this case, the density of atoms forming the main body 3a and the like becomes higher in an order of those provided by the positive ion beam deposition process and the

negative ion beam deposition process. Namely, the electric conductivity becomes higher in this order, and the electric field emitted becomes lower in this order. Such a difference between densities of atoms is due to the reason that the internal potential energy (electron affinity) of negative ions is lower than the internal potential energy (ionization potential) of positive ions.

Particular examples will be described below.

The formation of the main body 3a and the surface layer 3b can be carried out using the ultra-high vacuum type negative ion beam depositing apparatus shown in Fig.2.

To form the main body 3a, a process was employed which comprises, as in the first exemplary embodiment, the steps of (a) applying a predetermined value of voltage to each of portions of the apparatus, (b) producing positive ions of cesium (Cs) by the Cs plasma ion source 8, (c) sputtering the target 10 by the positive ions of cesium to produce negative ions of carbon or the like, (d) extracting negative ions by the negative-ion extraction electrode 12 through the suppressor 9 to produce a negative ion beam 17, (e) converging the negative ion beam 17 by the lens 13, (f) removing electrons contained in the negative ion beam 17 by the electron remover 15, and deflecting only the negative ions toward the cathode plate 2 by the deflector 16.

The mass spectrum of the negative ion beam 17 is as shown in Fig.3. The primary negative ions in the negative ion beam 17 are  $C^-$  ions

having a constituent atom number of 1, and  $C_2^-$  ions having a constituent atom number of 2. However, the ion current of  $C^-$  is larger than that of  $C_2^-$ .

The main body 3a can be formed on the surface of the cathode plate 2 by the above-described process, as shown in Fig.10. Cesium phases are dotted as the metal element portions 23 at a plurality of points both inside of the main body 3a and at the interface 24 of the main body 3a with the surface layer 3b. The plurality of cesium phases dotted at the interface 24 as shown in Fig.11 are oxidized with the passage of time to form cesium oxide, and the projections 4 are formed from the cesium oxide.

Then, a negative ion beam depositing process similar to that described above can be carried out, such that a surface layer 3b made of an amorphous film of carbon is formed on the interface 24 of the main body 3a and bonded to the main body 3a. Thus, the surface layer 3b has a plurality of protrusions 25 formed to conform to the plurality of projections 4, as shown in Fig.8. A cold cathode element 3 produced in the above manner is defined as example B1.

For comparison, a main body 3a similar to the main body described above was formed on the surface of a cathode plate 2 by a process similar to the above-described process and left to stand in the atmosphere. As a result, substantially all of the projections 4 made of cesium oxide and dotted in the interface 24 were grown into a conical shape, as shown in Fig.12. A cold cathode element 3 produced from such a main body 3a is defined as example B2.

Table 3 shows conditions for forming the examples B1 and B2 by the negative ion beam depositing process.

Table 3

		Deposition energy (eV)	Extracting voltage (kV)	Voltage-current (V-A) of filament	Film forming time (hr)
Example B1	Main body	600	8	13.2-22	6
	Surface layer	200	10	13.6-22.4	1
Example B2		600	8	13.2-22	6

After formation of the main body 3a of the example B1, a substantially central portion of the main body 3a was subjected to a Raman spectroscopic analysis to examine whether the substantially central portion was amorphous. As a result, a broad Raman band was observed, as in Fig.4, and it was ascertained from this that the main body 3a was amorphous. Results similar to that in Fig.4 were also obtained for the surface layer 3b and the comparative example.

Photographs of the surfaces of the examples B1 and B2 were taken by an interatomic force microscope (AFM). Fig.13 is the photograph of the surface of the example B1, and Fig.14 is an enlarged tracing of an essential portion of the photograph shown in Fig.13. It can be seen from these Figures that a large number of protrusions 25 are dotted along the surface. In the case of the example B2, results similar to those shown in Figs.5 and 6 were obtained, and it was ascertained that a large number of conical projections 4 were dotted along the surface.



Further, the examples B1 and B2 were examined using a scanning electronic microscope (SEM) and as a result, the presence of cesium (metal element 23) in the inside of each of the examples B1 and B2 was observed.

Yet further, a secondary electron image on the surface of each of the examples B1 and B2 was photographed by Auger electron spectroscopy (AES). As a result, the presence of cesium on the surface of the surface layer 3b of the example B1 was not observed, but the presence of cesium on the surface of the example B2 was observed.

Yet further, the measurement of the emitted electric field was carried out for the examples B1 and B2 by a method similar to that described above (see Fig.7 and page 8, lines 6 to 14). As a result, the emitted electric field was of  $0.8 \text{ V}/\mu\text{m}$  in the example B1, and  $1.2 \text{ V}/\mu\text{m}$  in the example B2. Thus, it was ascertained that the example 1 had sufficiently low emitted electric field, as compared with the example B2.

Even when the main body 3a does not contain a metal element 23 as described above, a corresponding effect is provided.

The cold cathode element in each of the first and second embodiments may be applied to a flat panel display, a voltage amplifying element, a high frequency amplifying element, a high-accuracy close-range radar, a magnetic sensor, a visual sensor and the like.